THE USE OF HALLOYSITE FOR NUTRIENT AND MOISTURE RETENTION IN SOILS

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Environmental Engineering

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ABSTRACT

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Halloysite is a clay mineral with interesting properties that are applicable in many fields, such as nanotechnology and environmental remediation. Halloysite is a kaolin subgroup mineral, which has the chemical formula $Al_2Si_2O_5(OH)_2 \cdot 4\ H_2O$. Halloysite is an extremely interesting material due to its tubular nanoscale structure and its cation exchange capacity.

This study was done in order to determine whether halloysite, mixed in soil, would be helpful in retaining moisture or nutrients in the soil, and whether, through these properties, it would be useful for some practical application. The study was conducted by filtrating de-ionized water and chemical solution through peat samples containing different proportions of halloysite, and by using fast and slow flow rates. The parameters studied during the filtration test and analyses were pH, total dissolved solids (TDS), phosphate-phosphorus, nitrate-nitrogen and potassium, and the volume of water or nutrient solution retained.

The findings of this research showed that there is an increase in the retention of phosphate (57%), nitrate (14%) and potassium (16%) when halloysite is added in the peat. The reasons for the retention might be various, such as cation exchange, anion exchange and formation of precipitants, and this issue could be studied further. Out of the three elements, potassium was expected to be retained the best with halloysite in the soil, but in fact, it was phosphate retention that improved the most when halloysite was added, while the use of halloysite improved potassium and nitrogen retention approximately equally. Halloysite was also found to be helpful in moisture retention, especially when liquids are filtrating at a slow flow rate.

The ratio of halloysite in the soil is a very important variable, since halloysite easily forms an almost non-permeable layer in the soil.

Key words: halloysite, nanotechnology, cation exchange capacity, nutrients, filtration

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GLOSSARY

HNT	halloysite nanotube
TDS	total dissolved solids

1 INTRODUCTION

1.1 Halloysite and other minerals

Halloysite is a clay mineral consisting of two molecule layers with water in between. Halloysite is represented by the chemical formula $Al_2Si_2O_5(OH)_2 \bullet n\ H_2O$, in which n represents the number of water molecules between the layers (Sakiewicz et al, 2011). Usually n is 4 for halloysite. It has been found through research that halloysite can be used as an insulation material in environmental protection, as a coagulant for wastewater purification, as a catalyst and in nanocomposite technologies (Lutynski, Sakiewicz & Gonzales, 2014).

The structure of halloysite resembles minerals from the kaolin subgroup, the only difference with kaolinite being that halloysite has interlayer water between the molecule layers; n is 0 for kaolinite. Halloysite loses its interlayer water somewhat easily, so it is often naturally in a partly dehydrated state. Therefore, fully dehydrated halloysite is the same as kaolinite mineral. (Hillier & Ryan, 2002).

A single halloysite molecule is formed by Si-tetrahedral and Al-octahedra sheets (Lutynski et al, 2014). The Si-tetrahedral sheet, consisting of SiO_2, has oxygen on the outer surface, and therefore it has a negative charge. The octahedral sheet, consisting of hydrated Al_2O_3, has hydroxyl groups, out of which the hydrogen atom is the on the outermost, and therefore the charge of the octahedral sheet is positive. The Al-atoms inside the octahedral layer can be substituted, for example, with divalent atoms, such as magnesium or iron. (Sakiewicz et al, 2011; Abdullayev & Lvov, 2010). The cation exchange can therefore happen in both the octahedron layer and in the hydroxyl groups, as a replacement of hydrogen. (Chaikum, Sooppipat & Carr, 1981.)

These single halloysite molecules form planar structures, and furthermore, these structures will curl into nanoscale tubes. This kind of tubular structure is formed because of non-matching lattice structure between the Si-layers and Al-layers (Kamble et al., 2012). These halloysite nanotubes, HNT's, are approximately 0,5 µm long, have an inner diameter of 15 nm and outer diameter of 50 nm. The HNT's can be formed by 15-20 of these aluminosilicate layers rolled as one tube. (Abdullayev & Lvov, 2010)

Halloysite has been found to have some similar physical and chemical properties as bentonite. The term bentonite is somewhat wide; it refers to different clays that mostly consist of montmorillonite mineral and belong to the smectite group (Adamis, 2005). Bentonite has a little different type of structure than halloysite. A single bentonite unit is formed by two tetrahedral sheets that have one octahedral sheet in between them (Keijzer). Bentonite layers have weak bonds between the molecules and let water and ions easily, which makes bentonite to swell. (Sakiewicz et al, 2011.) Bentonite has been used as an insulation material in the environmental field, for which use halloysite is also suitable. The layers of halloysite molecules are easily dispersed but exposion to water does not cause halloysite to swell like bentonite. Halloysite is a very fine material with a high absorption capacity towards certain substances, such as heavy metals, for example, and it has a low permeability for liquids. Quite similarly, bentonite has a high sorption capacity (Carlson, 2004), has low permeability for liquids and high ability to cation exchange process. (Sakiewicz et al, 2011.)

Halloysite is characterized by its high affinity, or in other words, potential to atom substitution, to monovalent cations, such as K, Na, Li, Cs, especially in the octahedral layer. On the contrary, the affinity to multivalent cations, such as Ca and Mg is a lot less, even though Ca and Mg are cations with the charge of +2 and therefore the next closest to monovalent ions. Atom substitution causes layer separation between single halloysite molecules. Atom substitution happens more easily in halloysite than in bentonite, because in halloysite, there are three hydroxide groups in the octahedron layer, which can form bonds with other substances, instead of one free hydroxyl group in bentonite. Furthermore, in bentonite, cations have to reach the octahedron layer through the tetrahedral layer which makes substitution less likely.

Bentonite, mixed with soil or cement, has been used as a sealing material, Geosynthetic Clay Liners, for preventing contamination from spreading in the soil (Nathanail & Bardos, 2004). The suitability of bentonite for sealing nuclear waste repositories has also been researched in several studies during the past years. There are different types of bentonites according to their origin (Carlson, 2004) and same applies to halloysite. They can both also be chemically modified in different ways for several purposes.

It seems bentonite might have been researched more widely in more studies than halloysite and it is more familiar for somebody not being an expert in the mineral field. Therefore, it is rather natural to shortly mention also bentonite when describing halloysite or when comparing some of the properties of halloysite and bentonite.

The possible uses for halloysite nanotubes, HNT's, include for example acting as nanocontainers: storaging and releasing chemical agents (Abdullayev & Lvov, 2010) such as drugs, corrosion inhibitors and various macromolecules. In other words, HNT's are possible to be filled with ingredients that are slowly released and this feature could be useful in, for example, cosmetics, household and personal care products, pesticides and pharmaseuticals (Halloysite Nanotubes, 2015). It is also possible to use halloysite as a material for preparing different polymer-based composites and for catalytic conversion and processing of hydrocarbons. Furthermore, HNT's have been used for manufacturing high-quality ceramics, nanotemplates and nanoscale reaction vessels. (Rawtani & Agrawal, 2012.) The various nanoproperties of halloysite are possibly the most researched topic when it comes to the use of halloysite mineral.

1.2 Nutrients and soils

Plants can be grown in various soil materials, such as dirt, peat, sand, straw, wood-based materials, like coconut shell, and so on. Often, if the growing platform consists of coarse material such as blasted stone, a water-retaining layer is needed and it is made of clay or moraine (Rakennustietosäätiö RTS, 2010), since it holds moisture from draining due to gravity (Clay Minerals: Their Importance and Function in Soils, 1999).

Like mentioned in the introduction about halloysite and bentonite characteristics, clays generally have a good cation exchange capacity. Retaining water and nutrients is essential for growth in soils. As many of the nutrients are positively charged ions, clay-like materials, such as halloysite, could be considered as an additional material to be mixed with the soil for achieving a better platform for growth, for example.

There are 16 different elements plants need for growing and developing. Plants get three of them, carbon, hydrogen and oxygen, from atmosphere and soil water. The other 13 elements are nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, iron, zinc, manganese, copper, boron, molybdenum, and chlorine (Silva and Uchida, 2000). These elements the plants get from soil minerals, organic matter or either organic or inorganic fertilizers (Clay Minerals: Their Importance and Function in Soils, 1999). The 16 elements have been divided into different groups, primary macronutrients, secondary macronutrients and micronutrients, according to how much the plant needs them for growing. Nitrogen, phosphorus and potassium are the three primary macro nutrients for plants. (Tucker, 1999.)

Out of the essential elements mentioned, calcium, magnesium, potassium, iron, zinc, manganese, copper and boron have ions with a positive charge, and therefore, they are more likely to take part in cation exchange with halloysite. Table 1 shows the electric charges of these elements and the group these nutrients belong.

TABLE 1. The essential nutrient elements with a positive charge according to their nutrient group.

Element	**Charge**	**Nutrient group**
Calcium	2+	Secondary macro
Magnesium	2+	Secondary macro
Potassium	1+	Primary macro
Iron	3+	Micro
Zinc	2+	Micro
Manganese	2+, 4+, 7+	Micro
Copper	1+	Micro
Boron	3+	Micro

According to Table 1, the most important cations for plants are calcium, magnesium and potassium. It was mentioned earlier that halloysite has the strongest affinity towards potassium out of these three, which can also be expected due to the electric charge of potassium. Copper ions have the same charge, but they are micronutrients and are needed by plants only in small amounts.

1.3 Definition of the research question

The interest in this thesis is whether halloysite could be used as an additive in soils for some purpose, such as agriculture or growing platforms, to retain moisture and nutrients. Now, it is known which cation exchange, potassium, is the most likely to happen when halloysite is in contact with the cations of different elements. Therefore, the nutrients chosen to be researched were potassium, nitrate and phosphate. In the beginning of this research, the following research questions were set:

- If a chemical solution, i.e. a fertilizer, is poured through a halloysite-soil mixture, which nutrients out the mentioned are retained the best and how much is retained
- Whether these nutrients are retained better in halloysite-soil-mixture, in the soil itself
- How well the solution is retained in the halloysite or halloysite-soil mixtures compared to pure soil

The hypothesis for this research is that the use of halloysite in the soil will increase the retention of the nutrients, especially potassium, and moisture in the soil. A less supported guess is: if halloysite forms solid particles in the soil, it might even retain nutrients through other means than cation exchange, such as physically insulating them in the soil.

1.4 Aim of the work

The aim of this work is to make more basic study of halloysite and research its characteristics further. Also, one of the aims is hopefully to find a way to use halloysite for something productive.

2 THEORY

2.1 Bulk density

Bulk density is the ratio of the mass and bulk volume of the soil. Bulk volume is the volume occupied by a certain mass, including volume of the soil particles and the void spaces between them. Bulk density is expressed usually in g/cm^3.

Bulk density is defined in the following manner: a measuring can is used and its volume is defined by measuring the dimensions of the can. The can is filled with soil dried for one hour in 105 °C and the soil surface is made even by tapping the bottom of the can by hand. The can and the soil are weighed and the results are recorded and the mass of the soil sample calculated. Bulk density is then calculated according to Formula (1) below.

$$\text{Bulk density} = \frac{\text{Oven dry soil mass (g)}}{\text{Total soil volume (cm}^3\text{)}} \quad (1)$$

2.2 Total dissolved solids, TDS

Total dissolved solids, or TDS, is a term referring to the amount of charged ions in a given amount of water. Usually TDS is expressed in mg/L or ppm. The dissolved ions can be cations or anions, also from minerals, salts or metals, and the amount of these ions affects the quality of water. In pure water, what is not water molecules or suspended solids, they are total dissolved solids. (HM Digital, What is TDS? Read 26.4.2015.)

3 MATERIALS AND METHODS

3.1 Experiment set-up

A wooden funnel holder, consisting of 10 holes for funnels, was used for the filtration and formed the base of the experiment set-up. Nine slots were used at one time and nine 0,5-litre plastic bottles were placed upside down in the slots with their bottoms removed. For being able to filtrate 1000ml of filtrate through the soil samples, 10 byrettes were self-made out of 1,5-litre plastic bottles and by drilling a hole the bottle cap and the bottom of the bottle. A silicon hose and a tightener were attached onto the cap and sealed with hot-glue. The byrettes were attached in an upward position onto the funnel holder above the 0,5-litre bottles. A picture of the set-up can be seen in Picture 1.

PICTURE 1. The filtration experiment set-up.

The materials tested were physically modified halloysite from Poland, Silesian University of Technology, which is a Polish partner university of Tamk, and Biolan growth peat, the latter because peat is commonly used for cultivation. The halloysite had been dried at 80 °C for 6 hours, after that grinded in a ball mill and lastly screened in the appropriate fractions. The soil sample filtrations were carried out by gravity filtration in the bottle funnels. Halloysite is a very non-permeable material,

and therefore filtration through pure halloysite by gravity would not work and that was not done in this experiment. The method used is discussed further.

A few different filter material options for the funnels were tested to find out which one is the most durable for the purpose and does not affect pH and conductivity too much. After the tests, DeLaval fabric milk filters were found out to be the most convenient and suitable for infiltrating the chemical solution through the soil so that the chemicals are let through while the largest soil particles are not entering the filtrate solution. By measuring pH and conductivity before and after using the filter material, it was researched how much the filter lets particles through and effects the outcoming filtrate. The results of the filter tests without and with soil samples can be found from Appendix 1.

As halloysite has such fine particles, milk filters still let a part of them through, as can be seen from the results above. Therefore, before carrying out the spectrophotometer and AAS analyses, 10 ml syringes and 0,45 µm syringe filters were used for filtrating the solid particles from the filtrate.

The filtration test sets were planned to be done in three different flow rates. First plan was to use pumps with different flow rates and have 1 litre of nutrient solution, coming from a single bucket, fed through each sample. It was quickly seen that having 9 samples, setting enough pumps would have become quite challenging a set-up. In addition, it was not as easy to set up the flow rates accurately enough to be sure the same volume of solution has been pumped. Therefore, the feeding of the solution was simplified by using bottle byrettes.

The possibility of setting an accurate flow rate for the filtrate in this type of manual system was tested, but again, it was found out to be quite challenging. The flow rate would change quite a lot depending on how much filtrate is left in the byrette, if the hose was moved and how it was adjusted. Therefore, it was decided that instead of three test rounds, there would be two different flow rates, fast and slow one, which are adjusted to be approximately the same with each other. The adjustment of the flow rates was done manually each time and therefore has some variation, and so the fast and slow flow rates are averages of the flow times. Having two totally different flow rates still

makes it possible to see whether there is any difference in the results depending on roughly how slow or fast the filtrate is fed out of the funnels.

3.2 Chemical solution composition

Initially, the target elements of the research were phosphorus, nitrogen, sulphur, potassium, calcium and magnesium. The idea was to make a chemical solution including salts that contain these elements in known concentrations for being able to test the change in concentration after the filtration. It turned out to be rather challenging to use salts containing the mentioned elements in the same solution, as there would easily be some unwanted precipitate, such as calcium phosphate, forming. Therefore, the research was simplified and the number of elements decreased to N, P and K (and Na which was not a research parameter). The concentrations of the wanted nutrients in the solution were similar what tomatoes are given during harvest: the nitrate concentration optimally 180-300 mg/l, maximum 400 mg/l, phosphorus optimally 40-50 mg/l, maximum 70 mg/l and potassium optimally 300-500 mg/l, maximum 600 mg/l. (Farmit, Kastelulannoitus. Read 16.2.2015) The composition for 1 litre of the nutrient solution made is shown in Table 3.

TABLE 3. Composition of the chemical solution made.

Salt	Name	Molar mass (g/mol)	Amount (g)
K_2HPO_4	Potassium monohydrogen phosphate	174,18	0,3480
NH_4NO_3	Ammonium nitrate	80,04	1,4405
KNO_3	Potassium nitrate	101,11	0,6065
$NaNO_3$	Sodium nitrate	84,99	0,4255

1L of solution made contained 391 mg of K, 115 mg of Na, 62 mg of PO_4-P and 658 mg of N, out of which 406 mg NO_3-N and 252 mg NH_3-N.

3.3 Measuring equipment and analyses

The following devices were used for analyses: Mettler Toledo pH meter, Mettler Toledo conductivity meter, HACH spectrophotometer and atomic absorption spectroscope (AAS) .

3.4 Soil samples

For getting information about the densities of the soil materials, the bulk density of both peat and halloysite were measured. As the bulk densities of peat and halloysite differ a lot with each other, it was concluded that it is more relevant for the experiment to use equal masses of samples instead of equal volumes for all samples. Initially, it had been decided that pure peat, peat and halloysite mixture and pure halloysite would be the three sample types. After some quick testing it was found out that pure halloysite would not let any filtrate through, so simply pure peat and a mixture of peat and halloysite was decided to be used as sample types. Picture 2 shows how the crushed halloysite used for samples looks dry, it resembles dry silt according to how it looks. Peat was sieved with a kitchen sieve to achieve a more homogenous consistency.

An estimated peat and halloysite mass ratio, P:H, with a maximum amount of halloysite that would still let filtrate through, was 1:1. The second mixing ratio, with less halloysite, P:H was 7:3 and the last one 1:0. The total soil sample size was chosen to be 50 g for having a reasonable amount of soil material but letting the filtrate through in a reasonable time.

PICTURE 2. Dry halloysite used for samples.

The Biolan Growth Peat used includes some of the macro nutrients, and these concentrations will have to be taken into consideration when analysing the results. The nitrogen concentration in the peat is roughly 1000 mg/kg, phosphorus 600 mg/kg and K 3000 mg/kg (Biolan, Kasvuturve, last accessed 19.4.2015.)

3.5 Filtration tests

There were two sets of filtration experiments done: firstly, ion-exchanged water was filtrated through the mentioned soil samples, S1-S9, by using both fast and slow flow rates on two different rounds and samples were taken from each of them. Secondly, the same procedure was repeated by using the chemical solution, the so-called fertilizer, for filtration. Table 5 below shows the samples with their chosen ratios and the soil masses measured for the samples on each test round.

TABLE 5. Masses of the soil samples S1-S9 in each filtration.

		Water, fast		Water, slow		Nutrient, fast		Nutrient, slow	
Sample	**Ratio (P:H)**	**m peat (g)**	**m halloysite (g)**	**m peat (g)**	**m halloysite (g)**	**m peat (g)**	**m halloysite (g)**	**m peat (g)**	**m halloysite (g)**
S1	1:1	25,0	25,1	25,0	25,0	25,0	25,0	25,0	25,0
S2	1:1	25,1	26,0	25,0	25,0	25,0	25,0	25,0	25,0
S3	1:1	25,0	25,0	25,0	25,0	25,0	25,1	25,0	25,1
Avg. S1-S3		**25,0**	**25,4**	**25,0**	**25,0**	**25,0**	**25,0**	**25,0**	**25,0**
4	7:3	35,2	15,0	35,0	15,0	35,1	15,0	35,1	15,0
5	7:3	35,0	15,0	35,0	15,0	35,0	15,0	35,0	15,0
6	7:3	35,1	15,0	35,0	15,0	35,0	15,0	35,0	15,0
Avg. S4-S6		**35,1**	**15,0**	**35,0**	**15,0**	**35,0**	**15,0**	**35,0**	**15,0**
S7	1:0	50,0	-	50,0	-	50,0	-	50,0	-
S8	1:0	50,0	-	50,0	-	50,0	-	50,0	-
S9	1:0	50,1	-	50,0	-	50,0	-	50,0	-
Avg. S7-S9		**50,0**	**0,0**	**50,0**	**0,0**	**50,0**	**0,0**	**50,0**	**0,0**

After the experiment, the filtrate samples were collected either right after the de-ionized water in the byrette was finished or when the possible water layer on the soil sample had drained totally. Also the volume of the filtrated water or nutrient solution was measured and recorded.

4 RESULTS AND DISCUSSION

The results of the pre-tests of the soil material and filtration of the soil samples by using ion-exchanged water and nutrient solution are presented below.

4.1 Bulk density

Bulk density test results for halloysite and peat are shown in Table 6 below.

TABLE 6. Results of the bulk density measurements.

	Halloysite		**Peat (non-sieved)**		**Peat (sieved)**	
	Test 1	Test 2	Test 1	Test 2	Test 1 (wet)	Test 2 (dry)
Cup weight (g)	16,6	16,6	16,6	16,6	-	-
Cup volume (ml)	382,5	382,5	382,5	382,5	100,0	100,0
Soil + cup weight (g)	386,6	364,2	83,6	71,8	-	-
Soil weight (g)	370	347,6	66,9	55,1	23,8	24,1
Bulk density (g/cm^3)	0,967	0,909	0,175	0,144	0,238	0,241
Average bulk density (g/cm^3)	0,938		0,160		0,240	

The average bulk density for halloysite was 0,938 g/cm^3. According to Brown and Wherrett (last accessed 26.4.2015), the bulk density of clays is between 1,1-1,6 g/cm^3. The average bulk density measured for sieved peat was 0,240 g/cm^3, The bulk density of peat depends of the ash content, the decomposition degree and how much plant residues it has, and it is approximately 0,1-0,5 g/cm^3 (Jingming & Xuehui, last accessed 26.4.2015). According to these reference values, the bulk density measurements were quite well in correct range. The bulk density of peat is a lot less than halloysite bulk density. Like mentioned earlier, having two materials with such different bulk densities made it quite challenging to construct the soil samples so that halloysite and peat could be compared with each other. The method used was explained in Part 3.4 Soil samples.

4.2 Flow rates during filtration

The measured filtration times and the calculated average flow rates for filtrate on test rounds with de-ionized water and nutrient solution and fast and slow flow rates are shown in Table 7.

TABLE 7. Calculated average flow rates for filtrate on each filtration round.

	Water filtration, fast		**Water filtration, slow**		**Nutrient filtration, fast**		**Nutrient filtration, slow**	
Sample	**average filtration time for 1L (h)**	**flow rate (l/h)**	**average filtration time for 1L (h)**	**flow rate (l/h)**	**average filtration time for 1L (h)**	**flow rate (l/h)**	**average filtration time for 1L (h)**	**flow rate (l/h)**
1:1	2,65	0,42	7,36	0,14	2,10	0,48	7,36	0,13
7:3	1,93	0,55	6,71	0,15	1,92	0,54	6,92	0,15
1:0	1,77	0,57	6,47	0,16	2,01	0,50	6,22	0,16
ST. DEV.	0,38		0,38		0,07		0,47	
AVERAGE	2,12	0,51	6,85	0,15	2,01	0,51	6,83	0,15
		≈ 1L/2h		≈ 1L/7h		≈ 1L/2h		≈ 1L/7h

The filtration times for each soil sample were recorded so that it is possible to see how similarly the filtrations were carried out and how comparable the different filtrations were. The average flow rates of all filtrations went close to the wanted flow rates 1L/2h and 1L/7h, which was the most important target when setting the flow rates. The largest standard deviation in relation to filtration time was on the fast water filtration round, which means the filtrations were the least uniform and it might have an effect on some results. Still, the deviations in the analysis results are evened out by using the average results of each sample type. So, the most notable difference in the analysis results, that are presented next, does not come from the deviations in the filtration times of the same flow rate, but the difference lies mostly between fast and slow flow rate filtrations.

4.3 pH, TDS, nitrate, phosphate and potassium during filtration

The results for pH, TDS, nitrate, phosphate and potassium measurements are presented here. The results for all researched parameters are presented as averages of the three soil samples with same peat-halloysite-ratio, such as samples S1-S3 with ratio 1:1, that had either fast or slow flow rate and were filtrated by de-ionized water or nutrient solution. Therefore, these are shortly referred to as, for example, "fast water filtration" or "slow nutrient filtration". All the detailed results can be found in Appendix 2. All the measurements started at the point in which the liquid started filtrating through the soil sample and were finished when the whole solution had filtrated through the sample.

4.3.1 De-ionized water filtration

The results of the fast and slow de-ionized water filtration are presented in this section. The pH of the de-ionized water, used for both fast and slow water filtration, before filtration was approximately 6,6, conductivity approximately 9,1 µS/cm and TDS 5,82 mg/l. Figure 4 shows the results of pH measurements and Figure 5 the results of the TDS measurements.

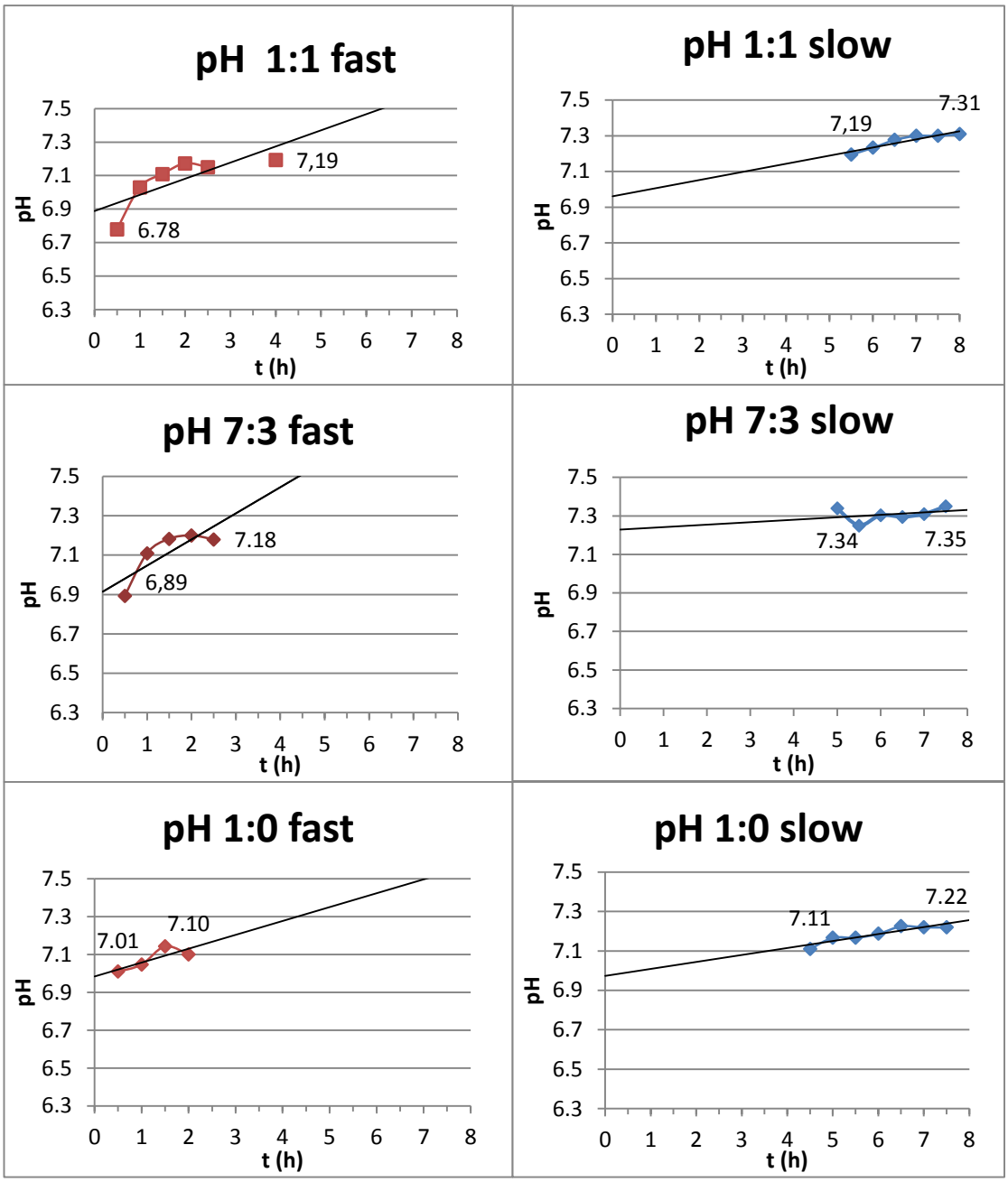


FIGURE 4. The average results of the pH measurements in relation to filtration time in hours.

The initial pH of the water being 6,6, it can be seen from Figure 4 that filtering the water through each soil sample raised the pH; fast flow rate faster, slow flow rate more constantly. The final pH was about 7,1-7,3. pH was slightly lower in the 100% peat samples (Figure 4) than in the samples containing halloysite. pH of the peat is about 6,5, similar to the de-ionized water, and should not change the pH a lot. It is challenging to say what causes the pH raise, since it seems to happen even without the halloysite present. The outer surface of halloysite tubes has pH 6-7 (Kamble et al, 2012).

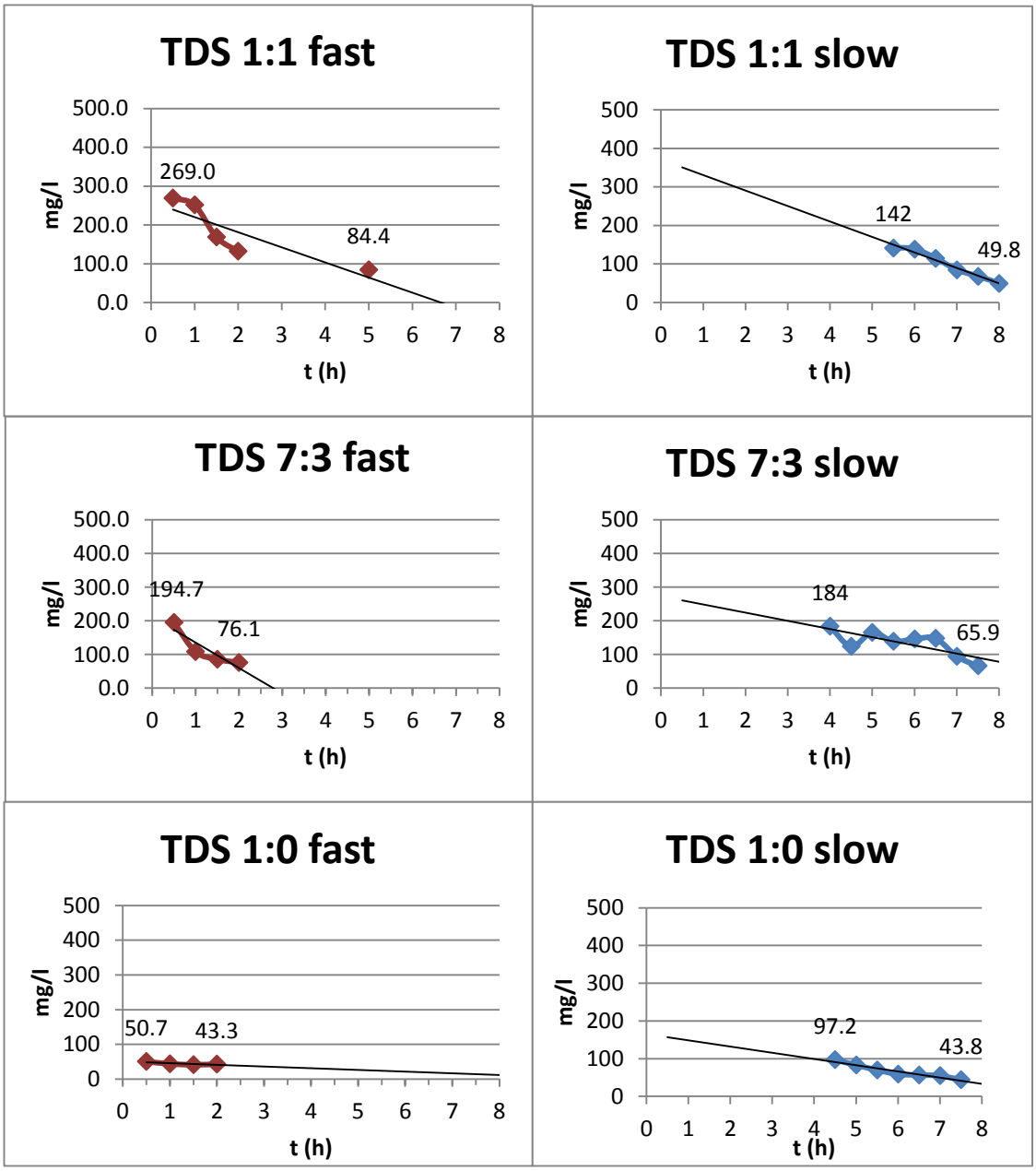


FIGURE 5. The results of the TDS measurements in relation to filtration time in hours.

The TDS values of the water filtration were quite low, since as an example, according to US. Environmental Protection Agency states that water with less than 500 mg/l is safe

for drinking (National Primary Drinking Water Regulations, 2009). The TDS values were highest in the fast filtration that had the highest ratio of halloysite. Therefore, the halloysite is probably leaching some charged ions, more than what peat does. The reason why TDS decreased in all of the samples could be that initially, a maximum amount of ions gets fast into the filtrate and the ions run out of the soil sample. Then, during the remaining filtration no more ions are introduced to the solution, and only the water is filtrating through and diluting the TDS concentration.

Figure 6 shows the results of the phopshate, Figure 7 the results of the nitrate and Figure 8 the results of potassium measurements for fast and slow water filtrations. De-ionized water had an initial phosphate concentration 0,08 mg/l and nitrate concentration 0,7 mg/l.

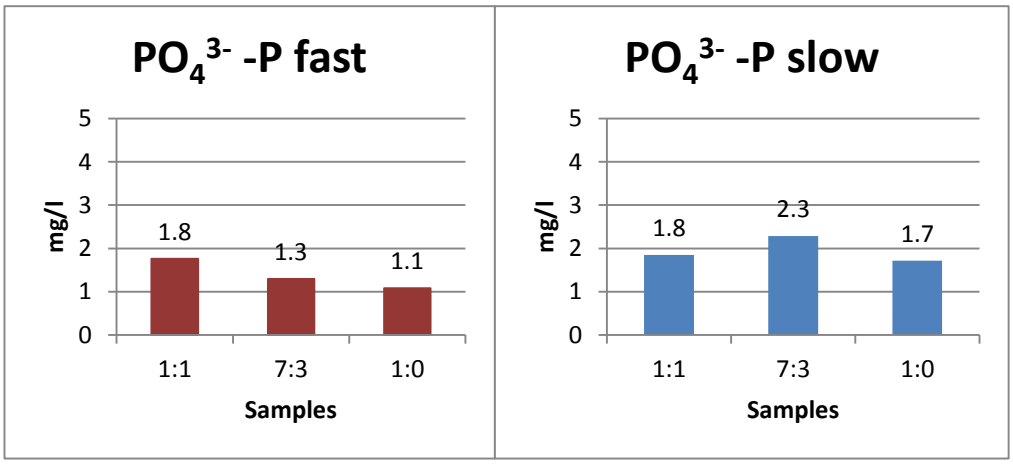


FIGURE 6. Phosphate measurement results of the fast and slow water filtration.

The phosphate concentrations increased nearly a neglectable amount after the water infiltration. The growth peat used has added soluble phosphate, so it could explain why some phosphate phosphorus concentration increase has happened. It was interesting that the highest phosphorus concentrations are in the two samples containing halloysite. The water filtrates through the halloysite-containing samples more slowly, so maybe it gives more time for the phosphate ions from the peat to dissolve in the filtrate. This would also be supported by the fact that generally, the concentrations were higher during the slow filtration. The leached phosphorus concentrations are really low, but it is relevant to remember that phosphate is a limiting nutrient and for example for plants: even a

small increase in concentration of phosphate can cause dramatic changes in the growth. (Lenntech, Phosphorus cycle. Read 26.4.2015.

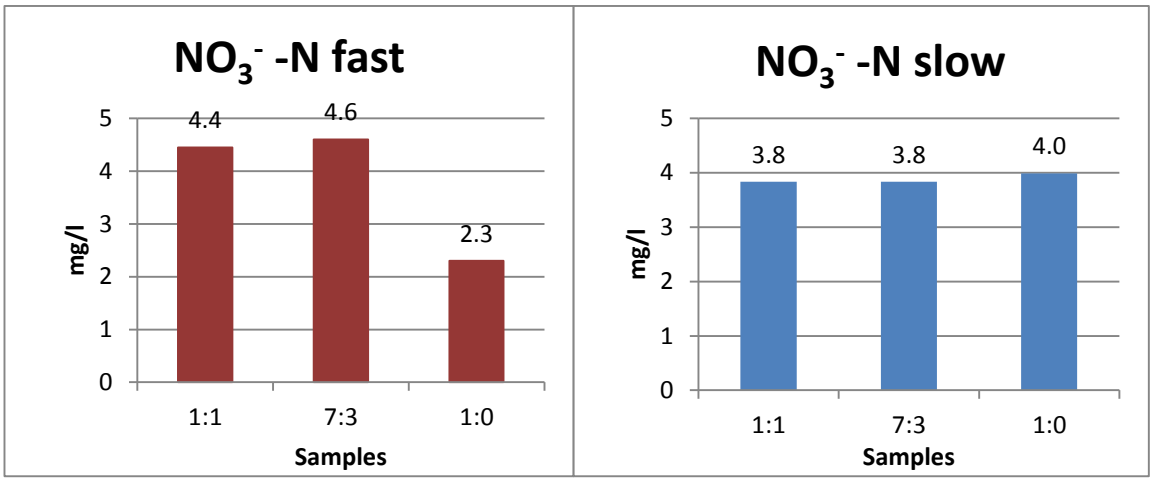


FIGURE 7. The average results for the nitrate measurement of the fast and slow water filtration.

Figure 7 shows that also small amounts of nitrate-nitrogen was leaching from the peat. Nitrate is also a limiting nutrient for plants and naturally it occurs in surface waters in lower than 1mg/l concentrations. In the effluent of wastewater plants it is possible to have 30 mg/l concentrations of nitrate. (U.S. Environmental Protection Agency, last accessed 26.4.2015.) Therefore, it is possible to say quite a lot of nitrate leached from the peat. During the fast filtration, the highest concentrations were in samples containing halloysite, but during the slow filtration the concentrations evened out between different sample types. More nitrogen leached out during the fast filtration than the slow one, which was the opposite occurrence compared to phosphorus. The reason for this is that phosphates have an attraction for soil particles, and nitrates dissolve more readily in water (U.S. Environmental Protection Agency, last accessed 26.4.2015.) The fast flow rate washes more nitrate-nitrogen into the filtrate probably because it flows with more power and has a larger volume of filtrate in the sample, to dissolve the nitrogen, at the same time.

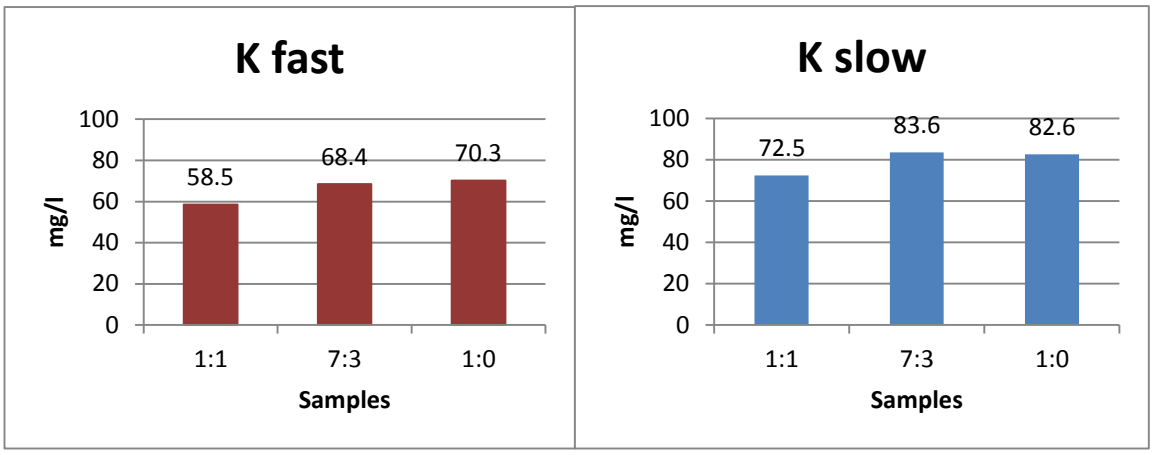


FIGURE 8. The average results for the potassium measurements of the fast and slow water filtration.

The initial concentration of potassium was the highest of the nutrients in the peat (3000 mg/kg). Therefore, it is not surprising that the potassium concentrations are quite high. In soil water, the dissolved potassium concentrations are about 5-10 mg/l. Potassium is retained by soils more easily than nitrate. (Shaw, Mechenic, & Klessig, 2004) Potassium does not leach from soils that contain enough clay and on the other hand, it has very weak attraction with organic particles, such as peat (Kelling & Schulte, last accessed 26.4.2015). The concentration of the leached potassium was the lowest in the sample with 1:1 P:H-ratio in both fast and slow filtration. The concentrations were higher during the slow filtration, for which the same explanation as for phosphorus might apply.

4.3.2 Nutrient solution filtration

The results of the fast and slow nutrient solution filtration are presented in this section. The start values in the nutrient solution were pH 8,0 and TDS 2015 mg/l. Figure 9 shows the results of the pH measurements and Figure 10 the results of the TDS measurements.

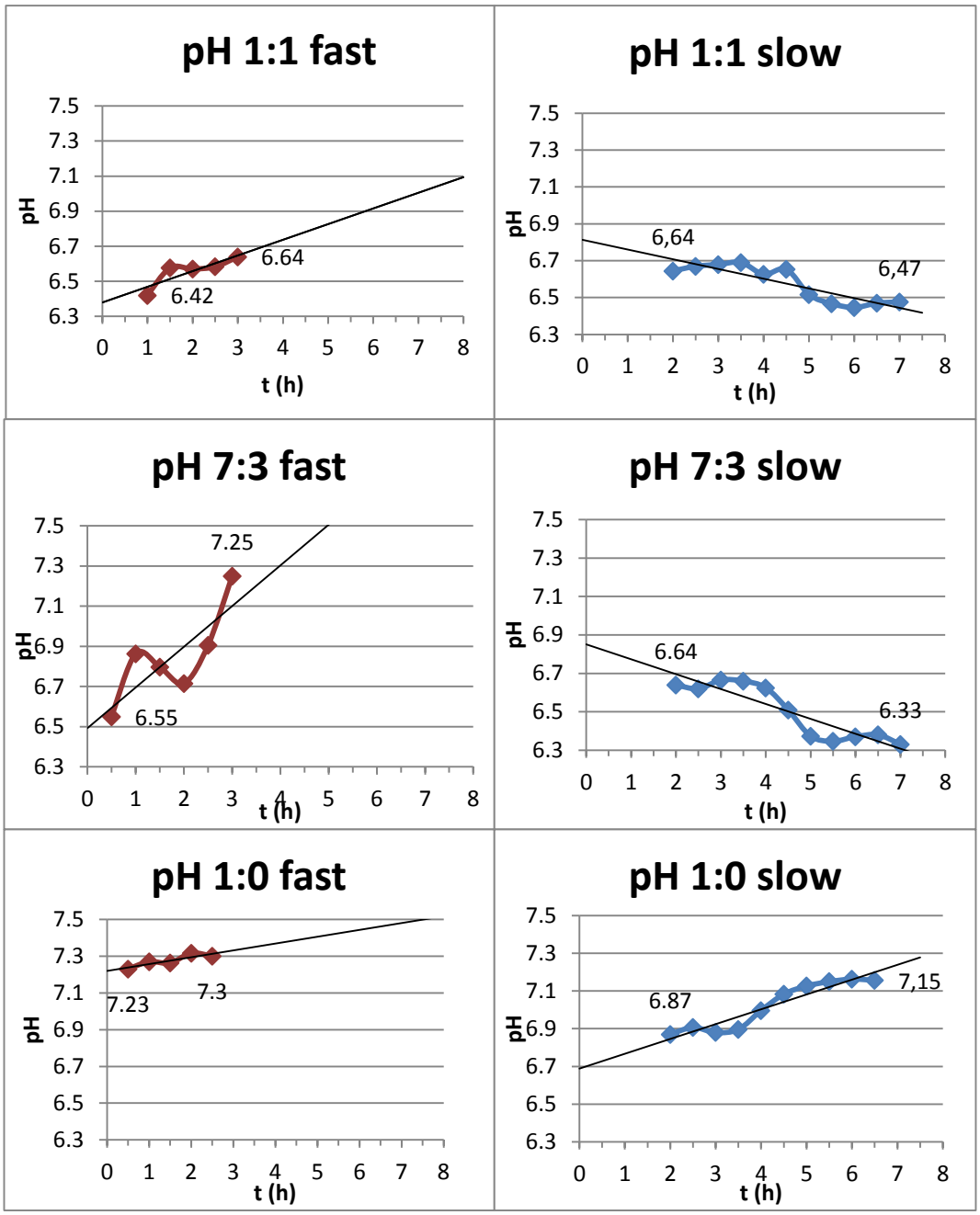


FIGURE 9. The average results of the pH measurements in relation to filtration time in hours.

The pH during the nutrient filtration was mostly lower than that of the water filtration. This is interesting, since the nutrient solution had initial pH 8, which is higher than the 6,6 of de-ionized water. During fast nutrient filtration, in which the solution was filtrating for about 2,5-3 hours in total, the pH was the lowest when there was the most halloysite in the sample. In other words, the peat contributes to the pH increase. Roughly, it is possible to see the pH behave similarly during the slow nutrient filtration until the time t (3). After time t (3), the pH decreases in the samples containing halloysite and raises in the peat sample.

Halloysite can exchange cations with, for example, the hydrogen in the hydroxyl groups. Between pH 3-12, halloysite has a negative charge, and is able to react with cations. The more pH is raised, the cation exchange capacity increases (Zao, Abdullayev & Lvov, 2014.) The possible explanation is that in the fast nutrient filtration, the pH is first raised by the peat and the nutrient solution. Then, after time t (3), the cation exchange starts happening in the halloysite. Cation exchange releases the hydrogen ions, which then lower the pH. This does not happen in the peat sample, and the pH keeps going up.

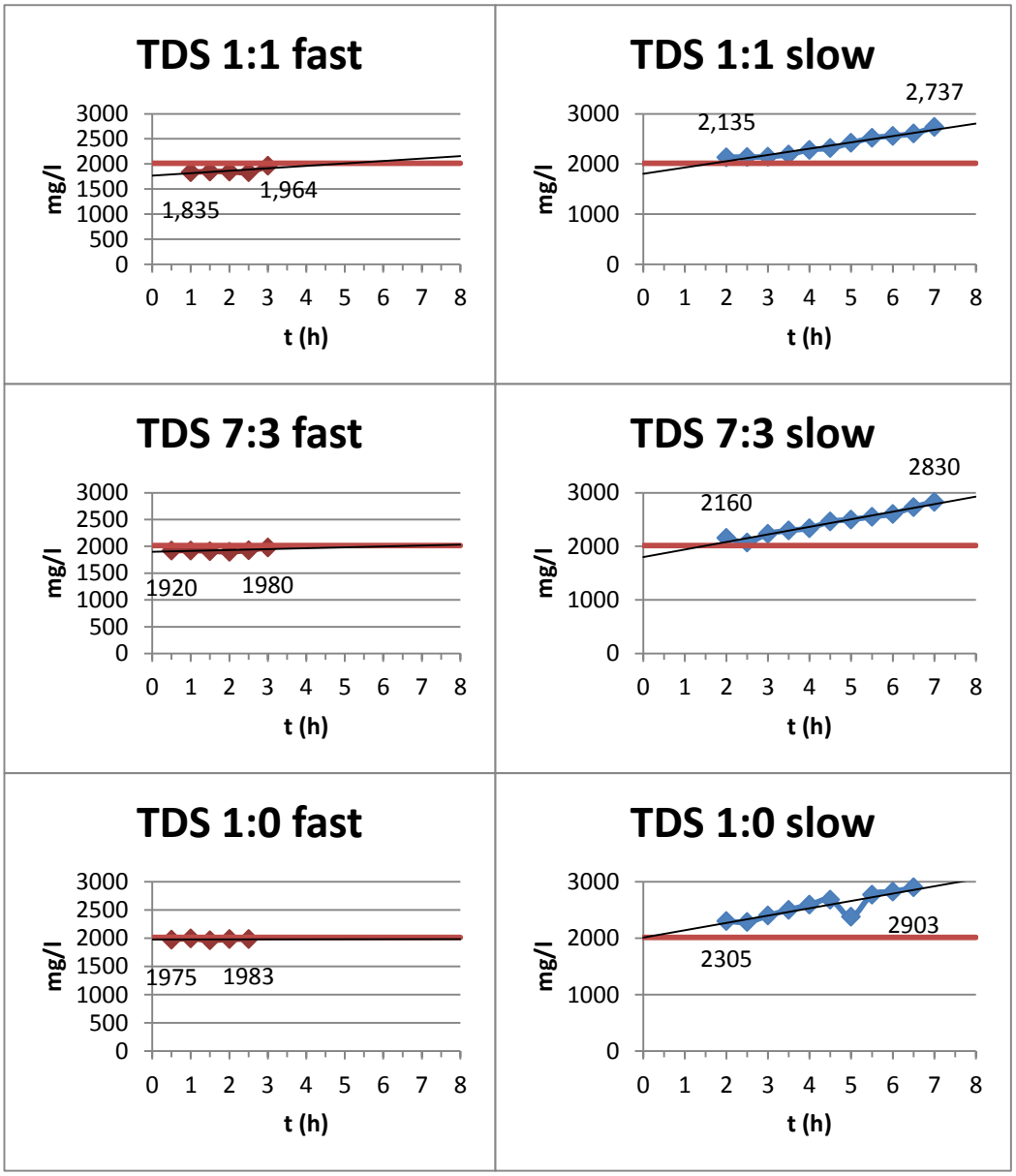


FIGURE 10. The average results of the TDS measurements in relation to filtration time in hours. The red line is indicating the initial TDS value in the nutrient solution.

Figure 10 indicates that the samples containing the most halloysite leached the smallest amount of ions during the fast nutrient filtration. All of the fast nutrient filtration samples contained less TDS than the initial 2015 mg/l, which is represented by the red line. From this, it can be concluded that peat slightly decreased the TDS from the original even by itself. Figure 10 shows the 1:1 sample had the largest change in TDS during filtration, then 7:3, and lastly, 1:0 had the least change. The same trend applied during slow filtration, but with larger concentrations of TDS than initially in the nutrient solution. The difference between fast and slow filtrations might be the longer retention time of the filtrate, which has time to be in contact with halloysite and peat and dissolves ions more effectively in the filtrate.

Figure 11 shows the results of the nitrate, Figure 12 the results of the phosphate and Figure 13 the results of potassium measurements after fast and slow nutrient solution filtrations. The initial concentrations of the nutrients were 62 mg of PO_4-P, 406 mg NO_3-N and 391 mg of K.

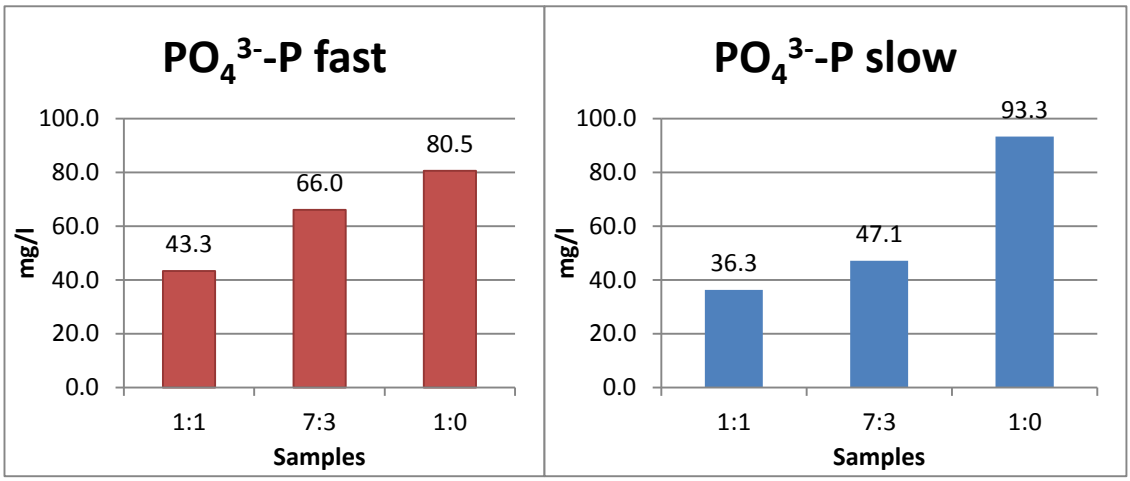


FIGURE 11. The average results of the phosphate measurements of the fast and slow nutrient filtration.

It can be seen in Figure 11 that after both fast and slow filtration, there is more phosphate phosphorus compared than the initial amount in the samples that have peat-halloysite ratio 1:0. That phosphorus is most likely leached from peat. The halloysite-containing samples had phosphorus concentrations close to the initial concentration in the solution or decrease in the concentrations. This would support the hypothesis that halloysite increases the retention of nutrients, such as P. Samples 1:1 and 7:3, the

samples containing halloysite, had smaller phosphorus concentrations after slow filtration compared with fast filtration, which is the opposite of what happened in the water filtration. The concentration in the peat sample was higher after slow filtration, which can be explained by the longer retention time during which phosphates have more time to dissolve into the solution.

Cation exchange might be a slow process, like mentioned earlier, and it seems easy to conclude this could explain the lower concentrations in the halloysite-containing samples during the slow filtration. But, phosphate is an anion, so it would seem quite surprising that any anion exchange would happen between halloysite and phosphate. Actually, according to Wilson (2013, 82) halloysite can uptake some phosphate, but it happens through another way than ion exchange. This phosphate uptake mechanism has to do with the hydroxyl groups in in the octahedral layer and aluminum phosphate precipitating.

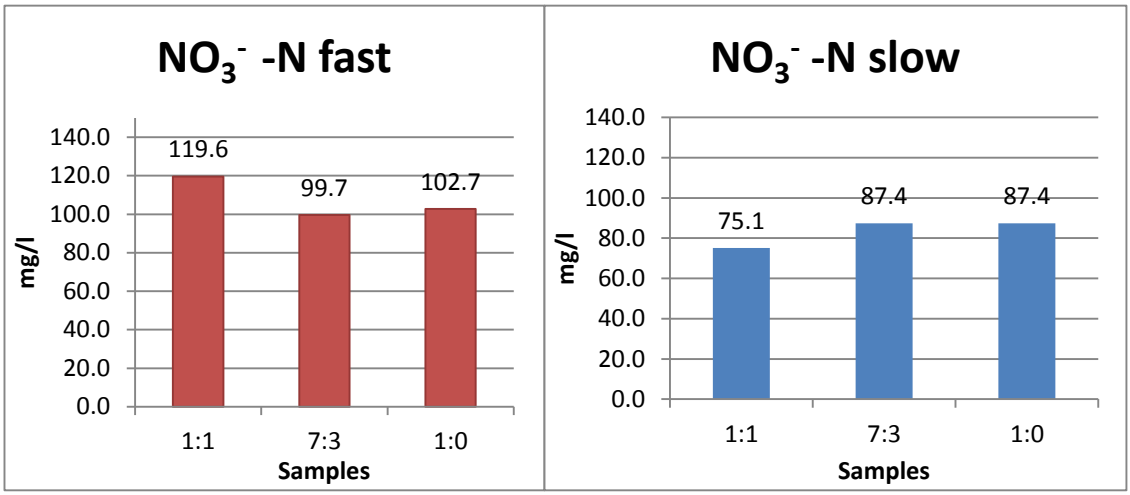


FIGURE 12. The average nitrate measurement results of the fast and slow nutrient filtration.

All the samples, including pure peat, during fast and slow nutrient filtration showed rather significant decreases in the nitrate-nitrogen concentrations (Figure 12) compared with the initial concentration. The results for the nitrate-nitrogen concentrations after the fast filtration behaved similarly as in the water filtration, 1:1 sample having the highest nitrogen concentration. The slow filtration was also similar to slow water filtration, the 1:1 sample having the lowest concentration. Apparently, a slow flow rate supports having less nitrogen leached from the soil. As nitrate-nitrogen readily dissolves in

water, rather than sticks into the soil particles, it seems like the slow flow rate gives time for some reaction to happen in halloysite, as the largest change in retention capacity was in the sample containing most halloysite.

In clays, there actually is anion exchange happening in addition to cation exchange. The anion exchange capacity exists due to the hydroxyl groups and increases with decreasing pH (Shell and Jordan, 1959, 303; Mohsenipour, Shahid, & Ebrahimi, 2015). Therefore, an explanation to the decreased nitrate-nitrogen concentrations and the better reduction while having the slow flow rate might be that in this experiment, there first happened cation exchange while the pH was higher. It takes time for the cation exchange to start, and after it starts, it slowly starts decreasing the pH. This was discussed earlier. As there generally happens some anion exchange in clays and they uptake nitrogen to some extent, it can be further concluded that the lowering pH during the slow filtration contributed to higher nitrate-nitrogen uptake than during the fast filtration. All in all, halloysite retains nitrate a little better than pure peat, and the nitrate retention improves with slow flow rates and a low pH.

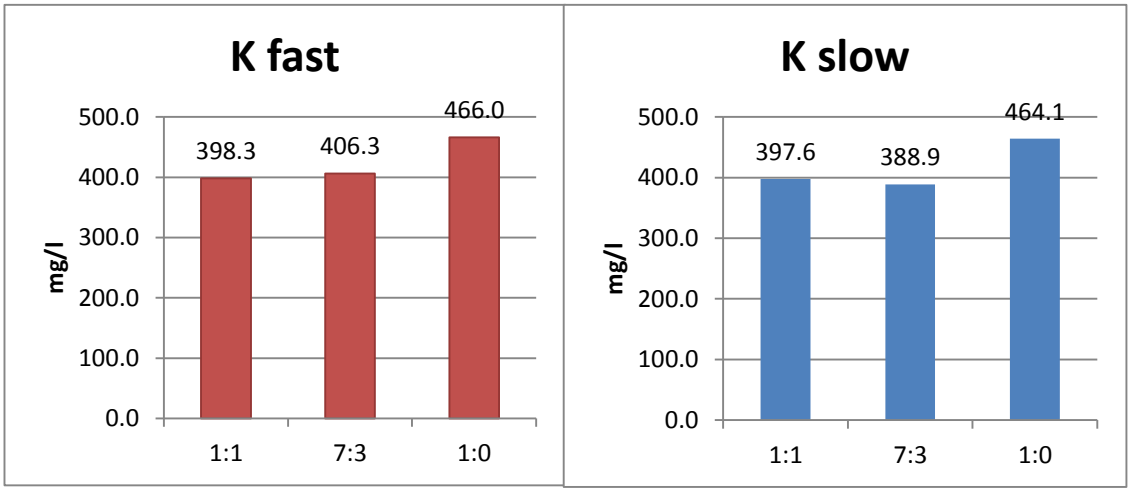


FIGURE 13. The average results for potassium measurements of the fast and slow nutrient filtration.

As Figure 13 shows, the potassium concentrations behaved somewhat similarly to de-ionized water filtration. Potassium ions were expected to take part in the cation exchange with halloysite. The concentrations after filtration are slightly higher than initially in the solution, but it is important to note that according to Biolan there can be even 3000 mg/kg (about 150mg in 50g of peat) of K in the peat, which was the highest amount of nutrient added in the peat. This can make it look like no potassium was

retained, though some retention probably happened. The concentrations between fast and slow filtrations are really similar with each other, which could indicate that the flow rate does not play such an essential role when cation exchange is happening in the soil.

4.4 Moisture retention

The quantitative and qualitative results for the moisture retention are presented in this section.

4.4.1 De-ionized water and nutrient solution retention as volume

The results for the moisture retention measurements are shown in Figure 14.

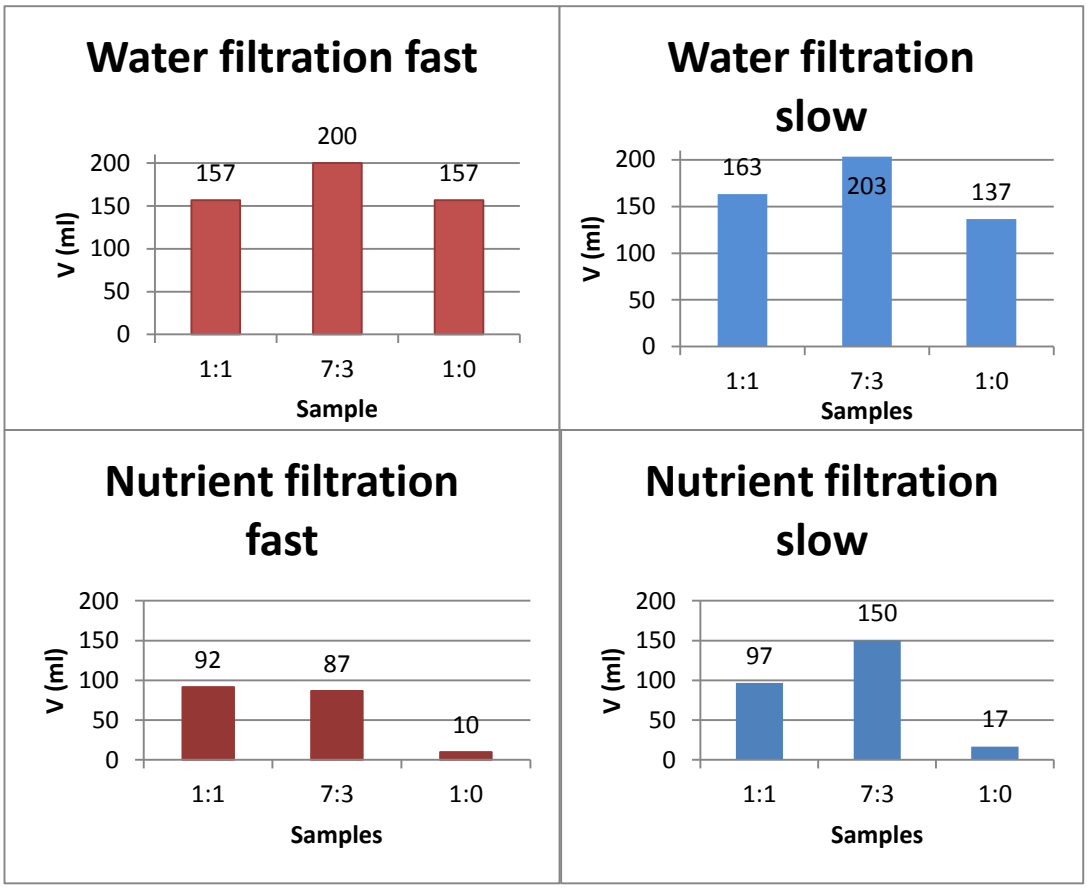
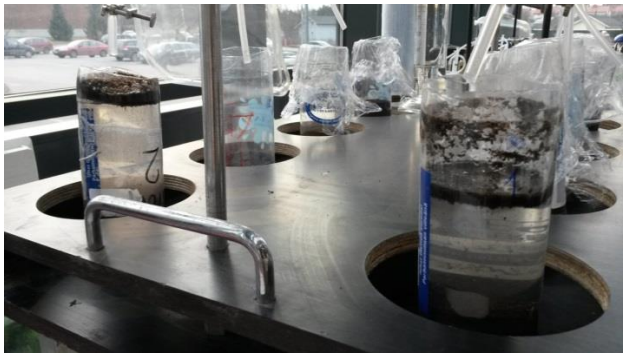


FIGURE 14. The evrage results of the moisture retention measurements for all filtrations. The volumes are the volumes of water or nutrient solution retained in the samples.

The volumes of water and nutrient filtration look quite different, but it is important to note the liquids were measured with different type of containers, so it might have

affected the comparability water retention of the water and nutrient filtration. The water filtration results are comparable, as well as nutrient filtration results. Generally, it seems that most water was retained on the slow filtration rounds. Furthermore, the 7:3 sample retained most water in three out of four filtrations. Also, in three out of four filtrations the two samples retaining most water are 1:1 and 7:3, which indicates halloysite does have a water-retaining effect when mixed in the soil. Picture 5 shows how slowly water filtrated through the 1:1 samples.



PICTURE 5. Water filtration through the 1:1 samples.

After filtration the samples were left in the bottle funnels for approximately one week, before the bottle funnels were emptied for next use. At the same time, it was possible to observe how much the samples had dried during that time. The peat samples came out dry and crumbling. Samples containing halloysite were still somewhat moist, and they came out of the bottles as a nice piece with a smooth, heterogeneous consistency. Picture 6 shows a halloysite-containing sample taken out of the bottle. This was a very vague observation, but supports the claims about halloysite helping to retain the soil moisture.

PICTURE 6. Halloysite-containing sample taken out of the bottle.

5 CONCLUSIONS

If taking into account all the samples with different peat-halloysite ratios, the average reductions from the initial concentrations in the nutrient solution were better for nitrate than phosphate. About 80% of nitrate was retained on average during the slow filtration and about 5% of phosphate during the slow filtration. Potassium, on average had an increase of 6,4% on average during the slow filtration. It can be concluded that slow filtration had the best retention rates in general.

The lowest concentrations for all nutrients were in halloysite-containing samples and the highest ones in peat-containing samples. The difference in percentage between the lowest and highest concentrations for each nutrient during slow filtration showed that retention of phosphorus was 57 % better when there was 50% halloysite (1:1) in the sample, there was 14% better retention of nitrogen when there was 50% of halloysite (1:1) and 16% better retention of potassium happened when there was 30% of halloysite (7:3). It is important to note that the Biolan peat used had added nutrients in it, which raises the total initial concentrations of the nutrients, and therefore the percentage reductions are likely to be higher in reality. The informed concentrations in the peat are quite rough estimations. Using those, it can still be concluded that the order of most overall retention was: nitrate, phosphate and potassium, the same as when compared with chemical solution concentrations.

In conclusion, there is increase in the retention of phosphate, nitrate and potassium when halloysite is added in the soil. The reasons for the retention might be various, such as cation exchange, anion exchange and formation of precipitants, and this could be studied further. Potassium was expected to be the best retained out of the three elements, but it turned out to be the worst out of the three nutrients. Phopshate retention improved the most when halloysite was added.

The results showed that when added to soil, halloysite can help retain moisture better in the soil. The flow rate had an effect: with fast filtration less moisture was retained. Halloysite also easily forms an almost non-permeable layer in the soil if there is too much of it, so the amount mixed in the soil is essential, for the soil not to become water-logged.

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APPENDICES

Appendix 1. Detailed results of the filter tests

TABLE 1. The results of the filter tests. CF stands for regular coffee filters, CC for cotton fabric and MF for milk filter fabric.

	pH before	**pH after**	**Conductivity before (µS/cm)**	**Conductivity after (µS/cm)**	**Outcome water out of 1L (ml)**	**Notes**
CF1	5,68	6,05	6,26	11,27	890	
CF2	5,94	6,19	7,04	10,16	870	Filter broke a little
CF3	6,28	6,46	8,21	10,91	880	
CF + 300 ml peat	-	-	-	-	-	
CC1	6,52	6,3	9,4	10,19	-	Outcoming water yellow
CC2	6,55	6,54	9,4	10,03	880	
CC3	6,57	6,58	9,25	9,86	880	
CC + 300 ml peat	6,65	6,6	9,21	126,3	690	
MF1	6,53	6,56	9,14	9,15	890	
MF2	6,58	6,57	9,05	9,03	900	
MF3	6,62	6,66	9,24	9,22	890	
MF + 300 ml peat	6,79	6,68	9,27	36,2	800	

Appendix 2. Detailed pH, TDS, N, P and K measurement results

TABLE 2. Fast water filtration; pH values in samples S1-S9 in relation to filtration time in minutes.

	pH								
t (mins)	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**
10									
20					6,71				
30		6,78		6,77	6,92	6,99		6,99	7,03
40	6,92	6,83		6,97	6,99	7,09	7,04	7,06	7,07
50	6,93	6,95		7,06	7,00	7,18	7,05	7,11	7,06
60	7,09	6,97		7,07	7,06	7,20	6,94	7,13	7,07
70	7,15	7,01		7,10	7,07	7,23	7,06	7,15	7,10
80	7,22	7,09	6,81	7,13	7,10	7,25	7,09	7,13	7,14
90	7,22	7,13	6,98	7,13	7,12	7,30	7,14	7,19	7,10
100	7,23	7,14	7,05	7,15	7,14	7,27	7,14	7,15	7,15
110	7,26	7,17	7,08	7,15	7,16	7,28	7,12		7,15
120	7,23	7,18	7,11	7,16	7,16	7,28			7,10
150	7,17	7,14	7,14	7,19	7,17				
240	7,13	7,14	7,31						

TABLE 2. Slow water filtration; pH values in samples S1-S9 in relation to filtration time in hours.

	pH								
t (hrs)	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**
3,5									
4						7,3			
4,5						7,25	7,11		
5					7,34	7,24	7,14	7,14	7,22
5,5		7,24	7,15		7,23	7,27	7,13	7,17	7,20
6	7,25	7,20	7,25	7,36	7,27	7,28	7,15	7,21	7,20
6,5	7,30	7,26	7,27	7,35	7,24			7,25	7,20
7	7,29	7,31	7,30	7,33	7,29				7,22
7,5	7,30	7,29	7,31	7,35					7,22
8	7,32	7,29	7,32						

TABLE 3. Fast water filtration; TDS values in samples S1-S9 in relation to filtration time in minutes.

	Total dissolved solids (TDS) (mg/l)								
t (mins)	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**
10									
20					165,0				
30		269,0		324,0	122	138,0		42	59,4
40	406,0	343,0		204,0	94,7	108,0	29,9	42,5	54,5
50	338,0	308,0		160,0	95,6	94,2	29,9	41,5	51,6
60	239,0	264,0		150,0	88,2	86,2	38,6	42,3	51,6
70	198,0	229,0		139,0	84,0	77,5	37,0	41,6	50,9
80	164,0	197,0	257,0	123,0	79,8	71,4	36,3	42,5	47,5
90	155,0	182,0	218,0	112,0	74,8	69,1	35,3	42,9	46,6
100	141,0	172,0	187,0	107,0	69,1	67,3	31,8	42,4	45,0
110	129,0	156,0	175,0	106,0	65,8	66,3	31,2		42,7
120	120,0	144,0	160,0	101,0	63,9	63,3			43,3
150	108,0	133,0	153,0	90,9	58,7				
300	72,7	96,0	89,1						

.

TABLE 4. Slow water filtration; TDS values in samples S1-S9 in relation to filtration time in hours.

	Total dissolved solids (TDS) (mg/l)								
t (hrs)	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**
3,5									
4						184,0			
4,5						124,0	97,2		
5					223,0	108,0	87,0	86,7	75,6
5,5		151	133,0		198,0	79,3	67,8	69,2	73,0
6	130,0	129,0	157,0	195,0	186,0	58,0	47,5	52,1	77,5
6,5	102,0	104,0	138,0	173,0	122,0			47,7	65,7
7	74,2	76,1	104,0	115,0	74,2				54,8
7,5	60,3	63,6	80,0	65,9					43,8
8	46,4	52,1	50,9						

TABLE 5. Fast and slow water filtration; P, N and K concentrations in samples S1-S9 after filtration

	Fast water			Slow water		
Sample	**PO_4^{3-} -P (mg/l)**	**NO_3^--N (mg/l)**	**K^+ (mg/l)**	**PO_4^{3-} -P (mg/l)**	**NO_3^--N (mg/l)**	**K^+ (mg/l)**
S1	2,9	3,7	43,6	2,0	4,6	70,1
S2	1,3	5,5	66,2	1,7	3,2	70,1
S3	1,1	4,1	65,8	1,8	3,7	77,2
S4	1,7	9,2	65,8	2,3	3,7	88,3
S5	1,2	2,3	67,4	2,3	4,6	82,0
S6	1,1	2,3	72,1	2,2	3,2	80,5
S7	0,9	1,8	67,5	1,7	6,0	82,9
S8	0,9	1,8	70,0	1,7	2,3	83,3
S9	1,5	3,2	73,3	1,7	3,7	81,7

TABLE 6. Fast nutrient filtration; pH values in samples S1-S9 in relation to filtration time in minutes.

	pH								
t (mins)	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**
10									
20									
30				6,84	6,26		7,29	7,13	7,27
40				6,82	6,33	7,43	7,28	7,14	7,29
50		6,27		6,75	7,30	7,36	7,25	7,10	7,27
60		6,4	6,44	6,68	6,55	7,36	7,31	7,20	7,30
70		6,54	6,53	6,69	6,46	7,37	7,31	7,20	7,29
80	6,65	6,54	6,53	6,66	6,37	7,35	7,29	7,24	7,30
90	6,71	6,57	6,45	6,66	6,41	7,32	7,29	7,23	7,27
100	6,68	6,55	6,47		6,39	7,29	7,33	7,38	7,33
110	6,71	6,54	6,49		6,55	7,31	7,30	7,30	7,31
120	6,72	6,52	6,47		6,17	7,26	7,31	7,32	7,32
150	6,77	6,53	6,45		6,52	7,29			7,30
180	6,79	6,59	6,54			7,25			

TABLE 7. Slow nutrient filtration; pH values in samples S1-S9 in relation to filtration time in hours.

	pH								
t (hrs)	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**
1,5									
2		6,72	6,57		6,64			6,8	6,94
2,5		6,74	6,6		6,62		6,93	6,84	6,95
3		6,73	6,63		6,57	6,76	6,87	6,8	6,97
3,5		6,75	6,63		6,59	6,73	6,94	6,81	6,94
4	6,61	6,61	6,66		6,63	6,62	7,04	6,86	7,09
4,5	6,62	6,67	6,67	6,46	6,52	6,55	7,05	6,99	7,21
5	6,49	6,56	6,5	6,29	6,4	6,43	7,07	7,05	7,26
5,5	6,45	6,51	6,44	6,30	6,35	6,39	7,08	7,09	7,28
6	6,4	6,49	6,45	6,32	6,37	6,42	7,08	7,11	7,30
6,5	6,43	6,51	6,47	6,35	6,39	6,40	7,07	7,11	7,29
7	6,44	6,51	6,48	6,33					
7,5									

TABLE 8. Fast nutrient filtration; TDS values in samples S1-S9 in relation to filtration time in minutes.

	Total dissolved solids (TDS) (mg/l)								
t (mins)	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**
10									
20									
30				1940	1900		1993	1964	1967
40				1929	1902	1917	1986	1968	1981
50		1826		1924	1916	1991	1949	1915	1991
60		1831	1838	1903	1895	1969	2010	1981	1996
70		1796	1793	1900	1871	1953	1987	1980	2010
80	1924	1812	1816	1896	1794	1962	1976	1959	1979
90	1911	1789	1854	1896	1845	1996	1972	1958	1957
100	1883	1827	1857		1844	1996	1974	1964	1983
110	1883	1841	1832		1865	1981	1980	1978	1996
120	1861	1836	1846		1809	1986	1971	1989	1989
150	1862	1810	1828		1871	1981	1974		1983
180	1970	1951	1970			1980			

TABLE 9. Slow nutrient filtration; TDS values in samples S1-S9 in relation to filtration time in hours.

	Total dissolved solids (TDS) (mg/l)								
t (hrs)	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**
1,5									
2		2090	2180		2160			2250	2360
2,5		2110	2170		2070		2310	2130	2420
3		2140	2150		2170	2300	2360	2400	2440
3,5		2180	2200		2260	2330	2450	2510	2550
4	2360	2230	2260		2330	2350	2560	2580	2640
4,5	2300	2350	2300	2560	2410	2420	2670	2660	2720
5	2430	2430	2400	2500	2500	2500	2320	2680	2140
5,5	2490	2550	2520	2590	2520	2550	2740	2770	2810
6	2560	2550,0	2570	2610	2590	2610	2790	2820	2860
6,5	2590	2610	2620	2660	2770	2770	2980	2870	2860
7	2700	2860	2650	2830					
7,5									
8									

TABLE 10. Fast and slow nutrient filtration; P, N and K concentrations in samples S1-S9 after filtration.

	Fast nutrient			Slow nutrient		
Sample	**PO_4^{3-} -P (mg/l)**	**NO_3^- -N (mg/l)**	**K^+ (mg/l)**	**PO_4^{3-} -P (mg/l)**	**NO_3^- -N (mg/l)**	**K^+ (mg/l)**
S1	38,3	133,4	418,0	37,0	92,0	404,4
S2	45,5	115,0	397,8	35,6	55,2	395,0
S3	46,2	110,4	379,1	36,3	78,2	393,3
S4	56,8	96,6	392,0	47,5	78,2	394,6
S5	71,3	105,8	393,3	44,2	105,8	381,7
S6	70,0	96,6	433,6	49,5	78,2	390,5
S7	78,5	92,0	457,2	74,6	78,2	466,4
S8	82,5	105,8	470,4	79,2	96,6	452,4
S9	80,5	110,4	470,4	126,1	87,4	473,6

TABLE 11. All moisture retention results in samples S1-S9.

	Liquid through sample (ml) after 1000 ml filtration			
	Water fast	**Water slow**	**Nutrient fast**	**Nutrient slow**
S1	880	860	850	880
S2	870	800	900	920
S3	780	850	975	910
S4	800	800	900	820
S5	800	790	900	890
S6	800	800	940	840
S7	800	830	990	980
S8	900	880	990	990
S9	830	880	990	980